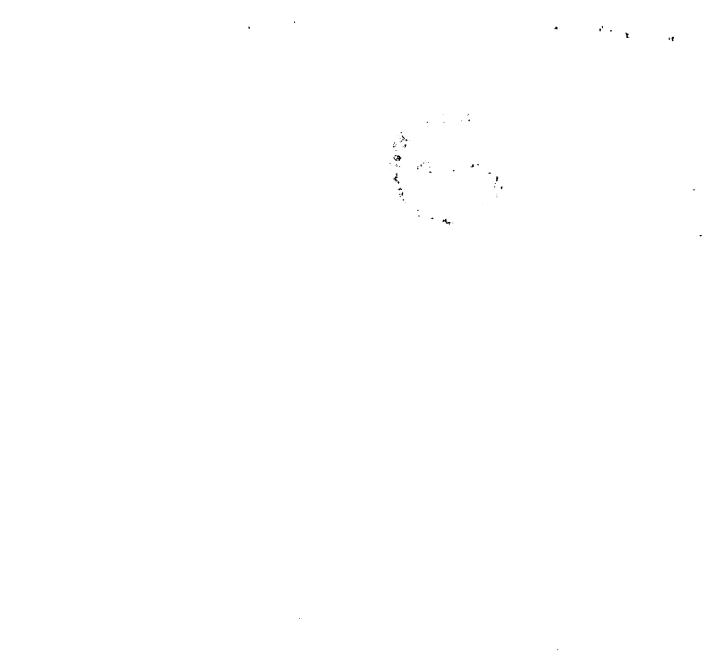
In re application of

Williams et al.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Art Unit: 1754

Serial No: 10/601,074 Examiner: Filed: June 20, 2003 For: FERTILISER **Commissioner for Patents** P.O. Box 1450 **Alexandria, VA 22313-1345** TRANSMITTAL OF CERTIFIED COPY Attached please find the certified copy of the foreign application from which priority is claimed for this case: Country: **United Kingdom** Application Number: 9902665.0 Filing Date: February 5, 1999 SIGNATURE OF ATTORNEY Reg. No. 26,725 Neil A. DuChez Tel. No. (216) 621-1113 RENNER, OTTO, BOISSELLE & SKLAR, P.L.L. 1621 Euclid Avenue Nineteenth Floor Cleveland, Ohio 44115 CERTIFICATE OF MAILING UNDER 37 C.F.R. § 1.8 I hereby certify that this correspondence (along with any paper referenced as being attached or enclosed) is being deposited on the below date with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231. Date: September 19, 2003









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Request for a grant of a patent

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(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help Newport you fill in this form) Gwent NP9 1RH Your reference 1. P006294GB CLM 2. Patent applicatio 9902665.0 (The Patent Offic. 5 FEB 1999 3. Full name, address and postcode of the or of each applicant Mandops (UK) Limited (underline all surnames) 36 Leigh Road, Eastleigh, Hampshire, SO50 9DT Patents ADP number (if you know it) If the applicant is a corporate body, give the country/state of its British 7597347007 incorporation. Title of the invention Foliar Fertiliser 5. Name of your agent (if you have one) D YOUNG & CO "Address for service" in the United Kingdom to which all 21 NEW FETTER LANE correspondence should be sent LONDON (including the postcode) EC4A 1DA Patents ADP number (if you have one) 59006 Date of filing 6. If you are declaring priority from one or more earlier patent Country Priority application applications, give the country and date of filing of the or each of number (day/month/year) (if you know it) these earlier applications and (if you know it) the or each application number Date of filing If this application is divided or otherwise derived from an earlier Number of earlier UK application, give the number and filing date of the earlier application (day/month/year)

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Agents for the Applicants

12. Name and daytime telephone number of the person to contact in the United Kingdom

Catherine Mallalieu

0171 353 4343

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FOLIAR FERTILISER

The present invention is concerned with compositions and methods of use which, as well as providing improved foliar fertilisation of plants, reduce the effects of various parasitic fungi on those plants.

Phosphorous is one of the essential major elements required by plants and it is usually supplied to plants in the form of phosphate and/or polyphosphate. Phosphates are the salts of phosphoric acid (having the formula H₃PO₄ and molecular weight of 98). In recent years, it has been shown that plants can obtain phosphorous from phosphonates (sometimes also referred to as phosphites) which are the salts (organic or inorganic) of either phosphonic acid or phosphorous acid (having the formula H₃PO₃ and molecular weight of 82). See, for example, USP nos. 5,514,200 & 5,830,255 to Lovatt; USP no. 5,707,418 to Hsu; USP no. 5,800,837 to Taylor. These describe formulations containing phosphorous acid or phosphonates suitable as fertilisers for plants. It has also been shown that phosphonate compounds are useful as fungicides, especially where the fungal organisms are phycomycetes or oomycetes. See, for example, USP nos. 4,075,324 & 4,119,724 to Thizy; USP no. 4,139,616 to Lacroix et al; USP nos 4,698,334, 4,806,445 & 5,169,646 to Horriere et al; USP nos 4,935,410 & 5,070,083 to Bartlet; USP no. 5,736,164 to Taylor. These describe formulations, containing phosphorous acid or phosphonates, suitable as fungicides for plants.

Ammonium thiosulphate and potassium thiosulphate, either alone or mixed with other liquid fertiliser components, have been used for many years as fertilisers. See literature on "Thio-sul"® and KTS® sulphur fertilisers produced by Tessenderlo Kerley. See also UK patent no. GB 2,259,912 to Sampson, which describes the use of ammonium thiosulphate in a plant growth stimulator.

The problems with the prior art are that the fertilising effect of phosphonate is less than might be expected from the amount of phosphorous applied, and the fungicidal effect is fairly limited in terms of the types of pathogen controlled. This is due to a complex mode of action involving a combination of some fungistatic action and natural plant defences coming into play (See Guest D I & Grant B R (1991) -The Complex action of phosphonates in plants - Biological Reviews 66, 159-187). The use of phosphonate, whilst

improving the resistance of plants to infections of downy mildew (eg *Plasmopora*) and *Phytophthora* diseases, does tend to increase the risk of ascomycete (eg *Erysiphe*) infections. The present invention seeks to provide a solution to those problems.

The present invention comprises using a mixture of a phosphonate together with either a thiosulphate, such as ammonium or potassium thiosulphate, or a salt of salicylic acid or salicylamide. The use of this combination shows a synergistic effect, in that the combination of phosphonate with thiosulphate or salicylate/salicylamide produces a greater fertiliser effect (plant growth) and fungicidal effect (reduction in pathogens) than the individual components used separately. In some trials, there was an even greater effect if all three components (ie phosphonate, thiosulphate and salicylate or salicylamide) were used together. The combination of thiosulphate with a salt of salicylic acid or salicylamide, in the absence of phosphonate, also produces healthy growth.

In a preferred embodiment, the compositions and methods of use of the invention include growth response effective and fungicidal effective amounts of a phosphonate, preferably in the form of either mono or dipotassium phosphonate (KH_2PO_3 , K_2HPO_3), and thiosulphate (preferably in the form of either ammonium or potassium thiosulphate -(NH_4)₂S₂O₃ or $K_2S_2O_3$) or a salt (organic or inorganic) of salicylic acid (preferably in the form of potassium salicylate or salicylamide - $C_7H_5KO_3$ or $C_7H_7NO_2$) or both a thiosulphate and a salt of salicylic acid or salicylamide, in aqueous solution.

The present invention is advantageous as it overcomes the aforementioned shortcomings associated with the prior art. Fertilisers based on the present invention provide a greater growth effective response than phosphonates or thiosulphates alone and the degree of fungicidal protection or resistance is broader than that achieved with phosphonates or thiosulphates alone. Plants treated with the present invention suffer less from phycomycete diseases (for example *phytophthoras* and downy mildews) than those treated with phosphonate alone and are also less prone to other parasitic fungi such as powdery mildews. Thus the present invention provides a means for applying a

single product to plants which is an effective fungicide as well as an effective fertiliser.

Another advantage of the present invention is that the formulation is very storage stable. Tests on mixtures of potassium phosphonate and ammonium thiosulphate stored for over one year have shown that there is no oxidation of the phosphonate to phosphate and the stored material shows no signs of cloudiness or precipitation. The use of organic acids as buffers (as in USP nos. 5,514,200 & 5,830,255) is not required to achieve stable solutions.

Phosphonates are produced by the neutralisation of phosphorous acid by alkalis. For instance when using potassium hydroxide for the neutralisation, depending on the molar ratio of potassium hydroxide to phosphorous acid, the phosphonate solution will contain varied amounts of di-potassium phosphonate, mono-potassium phosphonate and un-reacted phosphorous acid. We have found that a 42% w/w solution, having a pH of between 6.7 and 7.3 and containing approximately equal amounts of mono- and di-potassium phosphonate is a clear, colourless and very stable starting material for our present invention.

The most common form of thiosulphate is ammonium thiosulphate, and this is readily available commercially as a 60% w/w solution, with a pH of about 7.5 and a specific gravity of about 1.32. If a higher proportion of potassium is required in the final foliar fertiliser, the ammonium thiosulphate can be substituted, either partly or wholly, with potassium thiosulphate.

Salicylic acid itself has low solubility, but inorganic salts of salicylic acid, such as sodium or potassium salicylate are readily soluble. When salicylamide is used, rather than salicylic acid or a salicylate, the addition of a few drops of alkali assists in its solution, by forming sodium or potassium salicylamide. Salicylamide also dissolves more readily in the thiosulphate solution, the presence of small amounts of alkali or ammonia in the thiosulphate solution assisting in the solubilisation.

Varying amounts of each compound in aqueous solution may be blended together and, as is common with many foliar fertilisers, it is also possible to combine other fertilising elements, such as but not limited to, iron, copper, boron and molybdenum (often known as micronutrients) in the final solution. These

may be added as soluble inorganic compounds (eg sodium borate or sodium molybdate) or as chelates (eg copper EDTA) or other metal complexes.

When the final solution is to be applied to plants which, because of their hairy or waxy surface, may be difficult to wet, it may also be advantageous to include other additives, commonly known in the agrochemical industry, such as surfactants, wetting agents, spreaders and stickers. (Examples of wetting agents include silicone surfactants, nonionic surfactants such as alkyl ethoxylates, anionic surfactants such as phosphate ester salts and amphoteric or cationic surfactants such as fatty acid amido alkyl betaines).

The fertilisers produced according to this present invention are usually applied to the foliage of plants but may also be applied to the soil or added to the irrigation water. The fertilisers may be used advantageously on many types of agricultural and horticultural crops, including but not limited to, cereals, legumes, brassicas, cucurbits, root vegetables, sugar beet, grapes, citrus & other fruit trees and soft fruits.

Examples

So that the results obtained by using this present invention may be illustrated, the following examples of fertiliser solutions are included. These are for illustration purposes only and should not be construed as to limiting the scope of this present invention.

Solution 1

An aqueous solution containing a total of 30% by weight of mono and dipotassium phosphonate in roughly equal proportions.

Solution 2

An aqueous solution containing 55% by weight of ammonium thiosulphate ("ATS").

Solution 3

An aqueous solution containing 20 grams per litre of potassium salicylamide.

Solution 4

An aqueous solution containing 75 g/L mono potassium phosphonate, 75 g/L di-potassium phosphonate, 275 g/L ammonium thiosulphate and 10 g/L potassium salicylamide.

These solutions were applied to lettuce plants, both alone and in combination, and the applications were repeated after a 10 day interval. There were five replicates of each treatment and the results are presented as means of the five replicates. Five plants were also left unsprayed as an untreated control to the other treatments. After eight, twelve, sixteen and twenty-one days, the plants were examined for disease.

Table 1. Powdery Mildew Score (0 - 9, where higher number equals greater degree of disease)

Treatment (Applied initially and repeated 10 days later)	D	Days after first spray			
	8 days	12 days	16 days		
Untreated	4.0	6.6	7.2		
Solution 1 (1L/ha)	0.8	2.2	3.6		
Solution 2 (1L/ha	1.0	1.2	2.4		
Solution 3 (1L/ha)	1.6	3.2	4.2		
Solution 1 (1L/ha) + Solution 2 (1L/ha)	0.0	0.4	1.0		
Solution 1 (1L/ha) + Solution 3 (1L/ha)	0.4	0.6	1.0		
Solution 1 (1L/ha) + Solution 2 (1L/ha) + Solution 3 (1L/ha)	0.8	0.6	0.6		

Table 1 shows the synergistic effect on disease levels achieved by adding Solutions 1 & 2 (phosphonate + ATS) and between Solutions 1 & 3 (phosphonate + salicylamide) and the further effect of using all three solutions together. Disease levels were reduced from a mean of 7.2 to a mean of 0.6 As well as assessing disease levels, the growth of the plants was assessed by measuring the mean plant diameters after 35 days growth and by measuring the mean above ground fresh and dry weights.

Table 2. Plant Growth after treatment with the example solutions

Treatment (Applied initially and repeated 10 days later)	Amount of Rooting (0-9, 0= least rooting) - mean	Plant Diameter (mm) -mean	Above- Ground Fresh Weight (g) - mean	Above-Ground Dry Weight (g) - mean
Untreated	5.3	124	102.3	8.3
Solution 1 (1L/ha)	6.0	148	116.3	9.3
Solution 2 (1L/ha	5.3	160	109.0	8.7
Solution 3 (1L/ha)	4.7	150	104.7	8.5
Solution 1 (1L/ha) + Solution 2 (1L/ha)	6.7	144	119.0	9.5
Solution 1 (1L/ha) + Solution 3 (1L/ha)	6.7	170	120.7	9.7
Solution 1 (1L/ha) + Solution 2 (1L/ha) + Solution 3 (1L/ha)	6.7	168	131.7	10.6

Table 2 shows the synergistic effect on plant growth caused by adding Solutions 1 & 2 (phosphonate + ATS), Solutions 1 & 3 (phosphonate + salicylamide) and the further effect of using all three solutions together.

Claims

- 1. A fertiliser composition for stimulating healthy growth in plants comprising a mixture of a phosphonate with a thiosulphate.
- 2. A fertiliser composition for stimulating healthy growth in plants comprising a mixture of a phosphonate with a salt of salicylic acid or salicylamide.
- 3. A fertiliser composition for stimulating healthy growth in plants comprising a mixture of a phosphonate with both a thiosulphate and a salt of salicylic acid or salicylamide.
- 4. A fertiliser composition for stimulating healthy growth in plants comprising a mixture of a thiosulphate and a salt of salicylic acid or salicylamide.
- 5. A fertiliser composition for stimulating healthy growth in plants as claimed in Claims 1 to 3 where the phosphonate is an ammonium, sodium or potassium salt of phosphorous acid.
- 6. A fertiliser composition for stimulating healthy growth in plants as claimed in Claims 1, 3 or 4 where the thiosulphate is supplied as an ammonium, sodium or potassium salt.
- 7. An aqueous solution of a mixture as claimed in any one of Claims 1 to 6.
- 8. The use of a mixture as claimed in Claim 7 to treat agricultural and horticultural crops to stimulate healthy plant growth and crop yield by spraying the mixture onto the plants, the soil or applying the mixture with the irrigation liquid.

- A use as claimed in Claim 8 where the amount of phosphorous acid salt is
 150 g/ha to 2 kg/ha, the amount of thiosulphate is 250 g/ha to 6 kg/ha and the amount of a salt of salicylic acid or salicylamide is 1 g/ha to 100g/ha.
- 10. An aqueous solution of a mixture as claimed in Claim 7 substantially as described in the examples as Solution 4.
- 11. The use of a thiosulphate salt and/or a salt of salicylic acid or salicylamide to improve the stimulation of plant growth by a salt of phosphorous acid.
- 12. The use of a thiosulphate salt and/or a salt of salicylic acid or salicylamice to improve the control of parasitic fungi in plant growth or the resistance of plants to infections of parasitic fungi by a salt of phosphorous acid.
- 13. The use of a salt of salicylic acid or salicylamide to improve the stimulation of plant growth by a thiosulphate salt.
- 14. The use of a salt of salicylic acid or salicylamide to improve the control of parasitic fungi in plant growth or the resistance of plants to infections of parasitic fungi by a thiosulphate salt.

Abstract

Foliar Fertiliser

The present invention provides a liquid fertiliser comprising a mixture of a salt of phosphorous acid together with either a thiosulphate such as ammonium or potacsium thiosulphate and/or a salt of salicylic acid or salicylamide. The use of this combination as a foliar spray, soil drench or irrigation component produces a greater fertiliser effect (on plant vigour and growth) and greater resistance to or control of parasitic fungal diseases, than each of the components applied individually or any combination of just two components.

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